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Study of Polydispersity of Grafted Poly(dimethylsiloxane) Surfaces Using Single Molecule Atomic Force Microscopy

by

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Man-made polymers synthesized by free radical or polycondensation mechanisms are known to produce a wide distribution of molecular weights and hence characteristic chain lengths [1-5]. A quantity called 'Polydispersity Index' (*PI*) has been used as a rough guide to understand the distribution of these molecular weights.

$$PI = \overline{M}_w / \overline{M}_n$$

where $\overline{M}_w$ is the weight average molecular weight and $\overline{M}_n$ is the number average molecular weight. A polymer is considered to be monodisperse if *PI* equals 1. Different analytical methods, such as gel permeation chromatography (GPC) and combinations of light scattering and vapor pressure osmometry, are analytical tools that have been traditionally used to study the distribution of these different molecular weights (polydispersity) of polymers in solution [1-4]. On the other hand, there are few direct methods for analyzing lengths of molecules at surfaces [1, 4]. Given the importance of polymer adsorption in technologies ranging from adhesion, lubrication, to biology and medicine [1], new methods for characterizing polydispersity at surfaces are of both practical and fundamental interest.

Single molecule studies using atomic force microscopy may be able to directly characterize such surface polydispersity and this paper aims to examine that potential. Apart from the usual contact adhesion observed in AFM, polymer distortions can be observed when a grafted polymer chain bridges to the AFM tip [6-12] as can be seen in Figure 1. The suggestion that this phenomenon could be used to study polymer polydispersity has been suggested by several authors, [7, 8, 10b, 11] but has not been explored in detail.

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Single molecule atomic force microscopy (AFM) was used to study the statistical distribution of contour lengths (polydispersity) of polymer chains grafted to a surface. A poly(dimethylsiloxane) (PDMS) monolayer was grafted on a flat silicon substrate by covalently bonding Cl-terminated PDMS to an OH-silicon surface and characterized using contact angle measurements and ellipsometry, and single molecule AFM. A model for the single chain dynamics is presented. The statistical distributions of the polymer contour lengths were found to depend on concentration of the PDMS polymer used in the grafting solutions.

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